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# Influence of ionic strength and polyelectrolyte concentration on the electrical conductivity of suspensions of soft colloidal polysaccharides

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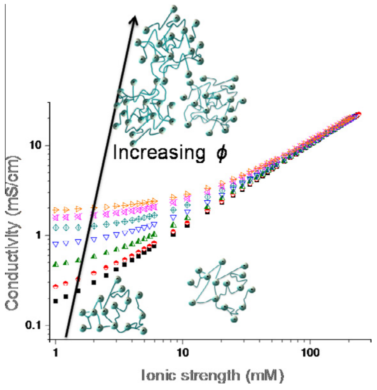
## GRAPHICAL ABSTRACT

Electrical conductivity measurements can be used for gaining information about the structure of soft particles even at high particle concentration where this electrokinetic technique proves to be very sensitive.



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## ABSTRACT

The electrokinetic properties of carboxymethyldextran, a soft and anionic polysaccharide, were analysed in aqueous $NaNO_3$ solutions through measurements of the electrical conductivity of the suspensions. The results, which furnish new experimental support for the structure of soft polysaccharides in electrolyte solution show that the polyion concentration governs the conductance behavior of the suspension as the ionic strength decreases. This is particularly evident for large polymer concentrations, for which electrical double layer overlap is more likely. In contrast, the electrical conductivity of the suspension at high ionic strength reduces to the contribution of the ions in solution, as screening of the polyion charges is more efficient in such conditions. The applicability of Ohshima's general conductivity expression to these electrical conductivity measurements was examined, and a major discrepancy against the theory was observed. The calculated values of the electrical conductivity deduced on the basis of this theory were found to be lower than the experimental ones. Possible reasons for this discrepancy are discussed and a numerical model, based on the use of a cell approach to account for hydrodynamic and electrical interactions between particles, has shown to be a good description of the experimental electrokinetic data.

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## 1. Introduction

Polymers with ionisable groups, also known as polyelectrolytes, have been the subject of intense research because of their fundamental importance in biological and biophysical processes [1]. Their remarkable interest originates from their physicochemical properties. In a polar solvent [2,3], their dissociation into polyions and counterions produces electrokinetic features that are governed by the electrostatic interactions between these charged species. The polyion–counterion interactions are strongly sensitive to some parameters such as the chain length [4], the charge density [5,6], the polyelectrolyte concentration [7,8], the counterion type [9,10], and the ionic strength [11–13]. Numerous theoretical and experimental studies, exhibiting the impact of these parameters on the features of polymer systems, are satisfactorily investigated by electrokinetic techniques, such as conductometry [14,15]. The description of charge transport properties of polyelectrolyte solutions depicts a relevant approach to provide useful information on the electrostatic polyion–counterions and hydrodynamic polyion–polyion interactions. Up to the present time, in spite of the amount of experimental data available in the literature, most investigations exploring the conductivity of polyelectrolytes in aqueous solution are devoted to hard particles bearing polyelectrolyte coatings [16–21]. As far as we know, there is almost no work in literature describing the electrical conductivity of concentrated suspensions of fully soft colloidal particles. In the present paper, an experimental investigation of the conductivity of carboxymethyldextran (CMD), a soft, anionic polysaccharide [22], is presented. The influence of the ionic strength and polymer volume fraction on the extent of polyion–counterion interaction and on the mobility of the polyelectrolyte species is analysed. The experimentally determined electrical conductivity values will also be compared with the general expression for the electrical conductivity of concentrated suspensions of spherical soft particles derived by Ohshima and a numerical model will be proposed. The investigation is intended to prove the validity of conductivity measurements in combination with a proper model for the characterization of the structure of these complex systems.

## 2. Experimental

### 2.1. Materials

The chemicals listed below were from analytical grades and used as received: $NaNO_3$ from Prolabo (Merck, USA); $HNO_3$, NaOH and $ClCH_2COOH$ from Aldrich (St. Quentin Fallavier, France). Ultrapure Milli-Q water was used in the preparation of solutions. Native Dextran T500, a biopolymer of bacterial origin from Amersham Biosciences (Uppsala, Sweden), was chemically functionalized by carboxymethyl grafting under alkaline conditions as described elsewhere [23–25] yielding carboxymethyldextran (CMD).

### 2.2. Characterization

The degree of substitution (DS), i.e. the amount of carboxymethyl groups per 100 glucopyranosidic units, and the volume charge density ($\rho_0/F$)of the synthesized CMD are determined by potentiometric titration at100 mM $NaNO_3$ ionic strength and pH7 (complete dissociation of the carboxylic sites). The hydrodynamic diameter ($D$) of the synthesized CMD and native Dextran T500, and their weight-average molar mass $M_w$ were measured at 25.0 ± 0.1 °C using a Zetasizer Nano ZS instrument (He–Ne red laser (633 nm), Malvern Instruments) and the multi angle laser light scattering coupled to steric exclusion chromatography (SEC–MALLS), respectively. Table 1 lists several properties of the native Dextran T500 and the functionalized carboxymethyldextran (CMD).

### 2.3. Sample preparation

Polysaccharide solutions were prepared 24 h prior to experiments in $NaNO_3$ electrolyte solution and stored at 4 °C to ensure the complete dispersion of polymers. All measurements were carried out at a temperature at 25 ± 0.1 °C.

### 2.4. Experimental method

DC electrical conductivity measurements were performed with a CD 810 Electronic Taccussel conductivity meter (France) equipped with a CM 02/55/G (Electronic Taccussel) parallel-plate conductivity cell using platinized platinum electrodes. The cell constant (equal to 0.88 $cm^{-1}$) was determined by calibration measurements with liquids of known conductivity from HANNA Instruments (Germany). The conductivity measurements were obtained at pH 7 by means of standard impedance measurements carried out at frequencies of 250 Hz and 1 KHz. 50 mL of polymer solution with known and constant concentration were titrated under magnetic stirring in initial electrolyte concentration of 1 mM $NaNO_3$. After each addition of 100 mM $NaNO_3$ used as the titrant, the conductivity was monitored until a stable value is reached. Several independent solutions were prepared, and runs were performed to ensure the reproducibility of the results. The accuracy in several conductivity measurements carried out is about 1%.

## 3. Results and discussion

### 3.1. Experimental data

Fig. 1 presents the evolution of the electrical conductivity of CMD with ionic strength in a wide range of polymer concentration from 0 g/L to 10 g/L at pH 7. The general shapes of these curves are similar to those of other polymer systems investigated in aqueous solutions and found elsewhere [26,27]. For all polymer concentrations tested, the electrical conductivity raises with the increase of ionic strength, but a closer inspection of the curves allows to distinguish two ionic strength regimes. Above salt concentrations of 60 mM $NaNO_3$, all data are nearly superimposed and vary linearly, meaning that polymer charge density has very little influence on overall conductivity, even for concentrated suspensions. Such a feature can be assigned to the fact that, in this ionic strength regime, polymer charges are strongly screened. The overall electrical conductivity is then mainly dependent of the small ions contribution.

In the second regime corresponding to the ionic strength range below 60 mM, the trends of variation clearly depart from that of high ionic strengths, the differences being more severe with decreasing ionic strength. This evolution of electrical conductivity clearly shows the very strong influence of polyion contribution as a result of a reduced screening of the polymer charges in this ionic

**Table 1**
Values of the degree of substitution (DS), volume charge density ($\rho_0/F$), hydrodynamic diameter ($D$) and weight-average molar mass ($M_w$) of the Native Dextran T500 and CMD at pH 7 in 100 mM $NaNO_3$.

| Polymer | DS(%) | $\rho_0/F$ (mol/m$^3$) | $D$ (nm) | $M_w$ (g/mol) |
|---|---|---|---|---|
| Dextran T500 | – | – | 40 | 794,000 |
| CMD | 49 | −38 | 58 | 634,800 |